



Saskatchewan
Research Council

**ON THE ORIGIN OF STRONG ACIDITY IN THE SNOW PACK OF NORTHERN
SASKATCHEWAN**

by

**J.V. Iribarne
University of Toronto
Toronto, Ontario**

and

**S.R. Shewchuk
Saskatchewan Research Council
Saskatoon, Saskatchewan**

SRC Technical Report No. 186

Publication

E-906-39-B-85

October, 1985

ON THE ORIGIN OF STRONG ACIDITY IN THE SNOW PACK OF NORTHERN
SASKATCHEWAN

by

J.V. Iribarne
University of Toronto
Toronto, Ontario

and

S.R. Shewchuk
Saskatchewan Research Council
Saskatoon, Saskatchewan

SRC Technical Report No. 186

SRC Publication No. E-906-39-B-85

October, 1985

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	(ii)
LIST OF FIGURES.....	(iii)
LIST OF TABLES.....	(iii)
LIST OF APPENDICIES.....	(iii)
INTRODUCTION.....	1
PROCEDURE.....	5
RESULTS.....	14
DISSCUSSIONS AND CONCLUSIONS.....	26
RECOMMENDATIONS.....	31
ACKNOWLEDGEMENTS.....	33
REFERENCES.....	34
APPENDICES	35

ABSTRACT

Snow cores were collected from two sites in northern Saskatchewan and analysed for organic ions. The primary site was the Haultain Lake area and the background site was the Wollaston Lake area. A complete ion balance was conducted on the individual snow cores. Significant inorganic anion deficits were found in most of the samples analysed. The one clear explanation of this is the presence of organic anions. These organic ions can be considered, in part, related to acids. The specific organic ions identified were formate, acetate, oxalate and propionate. The propionic ion was clearly the most dominant. The variation of organic ions is irregular and spotty in the snow chemistry at Haultain Lake. However, at Wollaston Lake organic anions made a significant contribution to the ion balance.

LIST OF FIGURES

	<u>Page</u>
Figure 1. Plan view of the Haultain Lake site with location and numbering system for snow cores.	6
Figure 2. Plan view of the Wollaston Lake site with location and numbering system for snow cores.	7
Figure 3. A Gran plot titration for snow sample number 22.	16
Figure 4. The observed conductivity vs the calculated conductivity	17

LIST OF TABLES

Table 1. Latitude and longitude coordinates of the sites	5
Table 2. Acidity and conductivity measurements of the snow cores.	15
Table 3. The concentration of cations in the snow (μ N)	19
Table 4. The concentrations of inorganic anions (μ N)	20
Table 5. The concentration of organic anions in the snow cores (μ N)	22
Table 6. A summary of the snow cores ion balances.	23

LIST OF APPENDICES

APPENDIX A - DISSOCIATION CONSTANTS OF SOME ORGANICS.	36
APPENDIX B - INFLUENCE OF CO ₂ ON pH MEASUREMENTS.	38
APPENDIX C - INFLUENCE OF CO ₂ ON CONDUCTIVITY MEASUREMENTS.	41
APPENDIX D - CONTRIBUTION OF CO ₂ TO WEAK ACIDITY.	43
APPENDIX E - GLASSWARE.	45
APPENDIX F - A SEPARATE SERIES OF DETERMINATIONS ON A COMPOSITE SAMPLE FROM HAULTAIN LAKE	49

INTRODUCTION

Strong acidity has been observed in the snow pack of northern Saskatchewan. The origin and nature of this acidity has not been completely understood. Due to a large and consistent inorganic anion deficit (Shewchuk, 1982) it is not possible to understand the source of this acidity because an accurate solution of the ion balance could not be conducted. It is the purpose of this study to further quantify the extent of the acidity and to determine if organic acids are making a contribution to the total ion balance.

It has been shown that organics as natural acids do exert a major control of acidity in precipitation at some remote locations (Galloway, 1983). These organic acids may contribute to free acidity of natural precipitation, particularly in the cloud processes (Chameides et al, 1983). In addition, other natural species may contribute to free acidity in precipitation. In northern Saskatchewan significant amount of strong acidity has been found in the snow (Shewchuk, 1983), but its origin is unclear.

There are several ways in which organic acids could be influencing the samples. Acetic acid for example accumulates in the environment when microbial respiration is anaerobic. Acetic acid has a significant amount of volatility. It can be adsorbed on the soil clays. Both Acetic and Formic acid have been observed in the gas phase in remote areas of the southwestern portions of the United States (Dawson et al. 1980). Oxalic acid may make up to 50% of the dry weight of leaves of plants (Stevenson, 1967). In addition, there are a great many other organic compounds present in the atmosphere in trace amounts, among them many acids. Nicholas (1973) lists a number of aliphatic acids as

volatile plant products, including formic, acetic, propionic, butyric and other acids of higher molecular weight. Lunde et al. (1977) have studied snow and rain samples from Norway, determining neutral and acidic compounds by gas chromatography-mass spectrometry. They list 45 acidic compounds. Thirty-five of them are long chain aliphatic acids, some of them dibasic. Dehydroabiatic acid was present in all but one of the samples. Phtalic, benzoic, hydroxy-benzoic, salicylic and other acids were also detected.

The conductivity of the melted snow, as in any ionic solution, is due to the conductances of the various ions present. If the ionic composition is completely known, the conductivity (or specific conductance) can be calculated from the ionic concentrations c_i and the equivalent conductances of the different ions λ_i . As melted snow is a very dilute solution (total ionic concentration is a fraction of $10^{-4}N$), the tabulated values of λ_i for infinite dilution can be taken with sufficient approximation. It is useful as a check on the ion balance to measure all the ions in snow, to calculate the conductivity, and to compare it to the measured value. In other words, conductivity provides another check on the internal consistency of the analytical results, but for that purpose it requires results of enough precision.

All the inorganic ions present in the samples are totally in ionic form; i.e., not as part of undissociated molecules. With organic acids, however, the situation is different. If we call HA any acid, its dissociation constant is

$$K = \frac{[A^-] [H^+]}{[HA]}$$

The concentration of anion $[A^-]$ contributed by this acid at the pH of the solution will be

$$[A^-] = \frac{[HA]}{[H^+]} K$$

when $[H^+]$ corresponds to the measured pH. The analysis of the sample gives the total amount of anion, whether ionized or not:

$$[A]_t = [A^-] + [HA]$$

Therefore, the contribution $[A^-]$ of that acid can be written

$$[A^-] = \frac{K [A]_t}{K + 10^{-pH}}$$

This is the concentration that has to be used in the calculation of the conductivity (K). The formula to be used is:

$$\begin{aligned} K = 10^{-3} & \left[\sum_+ c_{i+} \lambda_{i+} + (\sum_- c_{i-} \lambda_{i-})_{\text{inorg.}} + \right. \\ & + \frac{K_{\text{Fo}} [Fo]_t}{K_{\text{Fo}} + 10^{-pH}} \lambda_{\text{Fo}^-} + \frac{K_{\text{Ac}} [Ac]_t}{K_{\text{Ac}} + 10^{-pH}} \lambda_{\text{Ac}^-} + \frac{K_{\text{Pr}} [Pr]_t}{K_{\text{Ac}} + 10^{-pH}} \lambda_{\text{Pr}^-} + \\ & \left. + [Ox]_t \lambda_{\text{C}_2\text{O}_4^{=}} \right] \end{aligned}$$

In this formula, the factor 10^{-3} is a conversion of cm^3 to liter, the c_{i+} 's and c_{i-} 's are the concentrations (in normality) of inorganic cations and anions, respectively, the λ_{i+} , λ_{i-} and $\lambda_{\text{A-}}$ are the equivalent conductances at infinite dilution, in $\text{cm}^2\text{S}/\text{eq}$, of the respective

ions, A⁻ meaning Fo⁻ (formate HCOO⁻), Ac⁻ (acetate CH₃COO⁻), Pr⁻ (propionate CH₃CH₂COO⁻) or Ox⁻ (oxalate C₂O₄⁼).

In this study we are concerned with acids that can contribute to the acidity of the snow, as measured by its pH when melted. Only some of the acids mentioned in the quoted bibliography may be dissociated to an extent that they may contribute to the measured pH.

Considering that these acids are probably present in concentrations comparable with the inorganic anions or smaller, one sees that acids with $K < 10^{-6}$ may be ignored for our purposes.

A number of aliphatic acids of low molecular weight, and of dibasic acids, have $K \geq 10^{-5}$ and are therefore possible constituents of interest. Long chain aliphatic acids, as well as many high molecular acids, have small constants and may be ignored (for example, K for abietic acid is 4×10^{-7} at 20°C; see Nyrén and Back, 1958). Some values of constants K for relevant acids have been collected in Appendix A for convenience. Acids that are partially dissociated ($K \geq 10^{-6}$) will contribute to the pH only with their dissociated fraction. This will be counted as "strong acidity" in the titration. The non-dissociated fraction will appear as part of the "weak acidity".

PROCEDURE

A light aircraft was flown into northern Saskatchewan to gather the snow core samples from two sites in the area. A small lake near Haultain lake was the primary site chosen because in past studies this area had shown a consistent amount of strong acidity in the snow (Shewchuk, 1983). The other site for this project was Wollaston Lake, selected for reference purposes. Samples were collected on March 20 and 21, 1985. The snow pack at this time had shown no signs of melting.

The exact locations for the snow chemistry lakes selected for study are given in past reports (Shewchuk, 1982 and 1983). A detailed schematic of the collection locations and the snow bag numbers taken are given in Figures 1 and 2.

Table 1. Latitude and longitude coordinates of the lakes.

Site	Latitude	Longitude
Haultain	56° 52'	106° 25'
Wollaston	58° 29'	103° 10'

At the Haultain, twelve cores were collected from the lake surface and four cores from nearby land. The land surface was heavily treed and the observers walked approximately 100 metres into the trees to

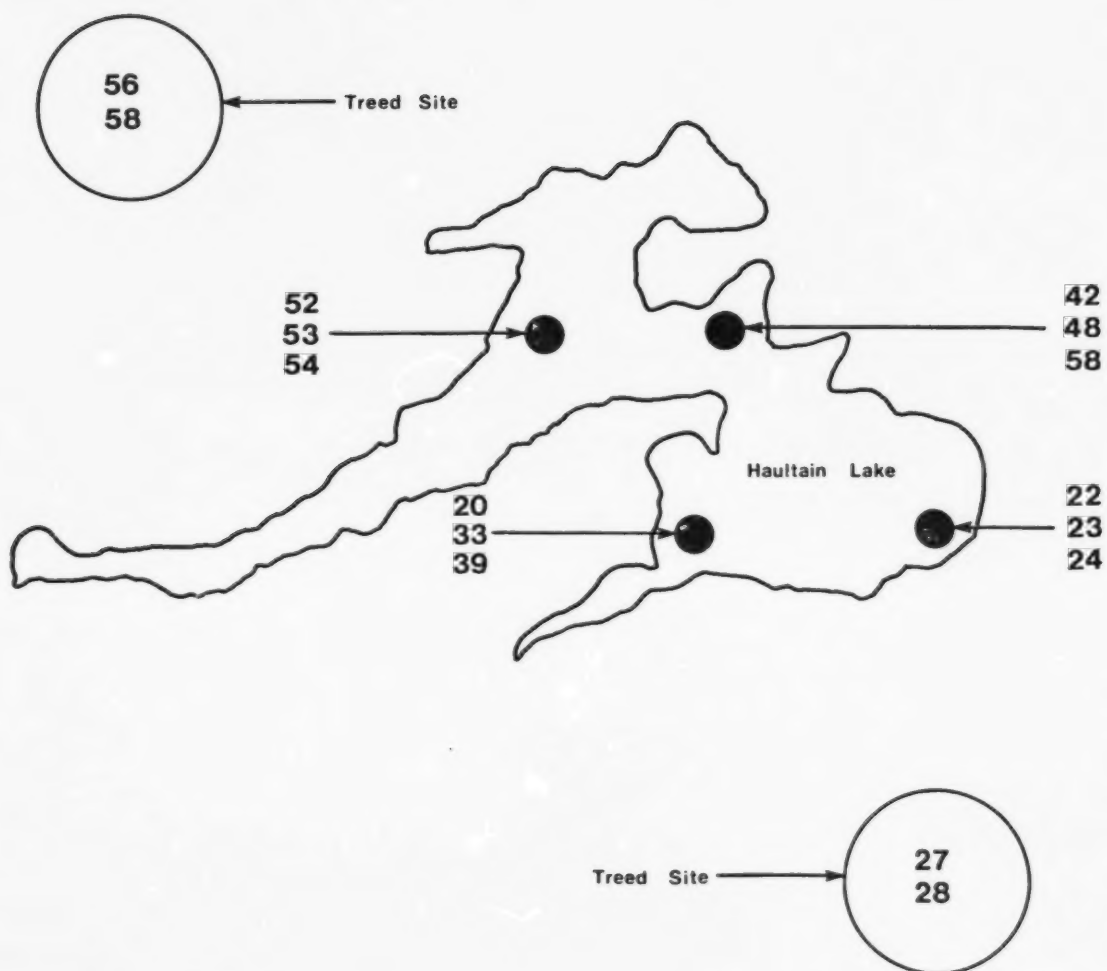


Figure 1. Plan view of the Haultain Lake with location and numbering system for snow cores.

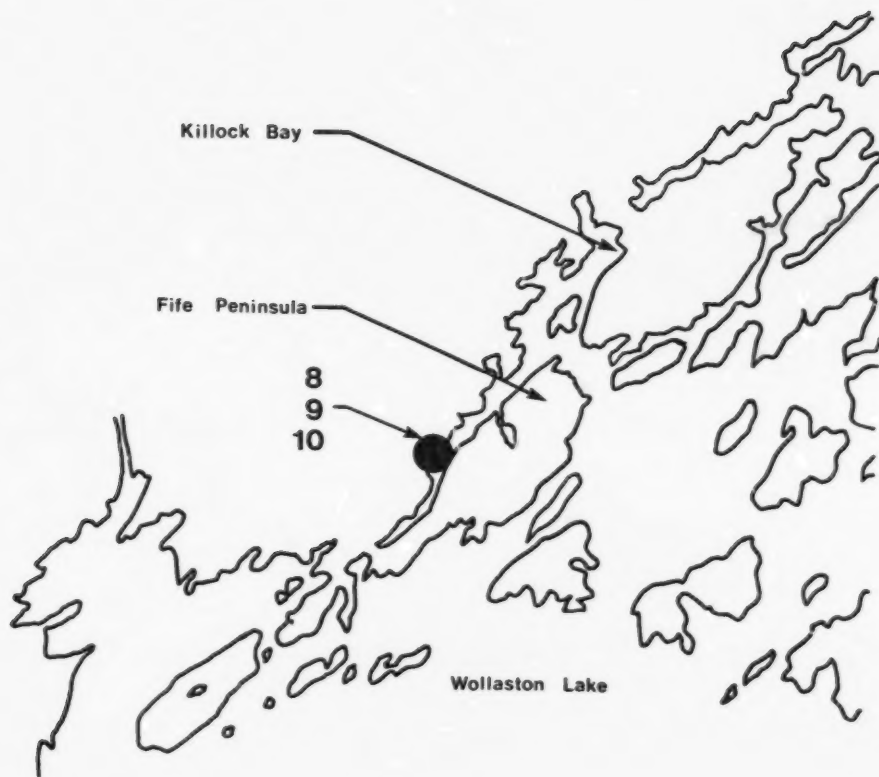


Figure 2. Plan view of the Wollaston Lake with location and numbering system for snow cores.

collect a sample. A great deal of emphasis was placed on getting a clean snow core sample from the treed areas. At Wollaston Lake three snow core samples were taken from the lake surface. The tree growth density at this site was much reduced from the previous site.

In order to address the question of what is the real variability of the sample chemistry, a separate analysis was conducted on each snow core.

Regarding the importance of organic acids, it was felt that to be able to appreciate it a good quality inorganic analysis was required, making possible the use of both ionic balance and conductivity to check on the consistency of results. In order to achieve this, it was essential to increase the accuracy of the results. For this reason, analyses were performed on pre-concentrated samples, and other improvements, such as titrating acidity in the absence of CO_2 , were introduced.

For convenience, all the concentrations quoted and tabulated are given in micronormality μN , i.e. in microequivalents per litre. If the equivalent weight of the species is E , the corresponding concentrations in ppm can be obtained by the simple relation

$$c(\text{ppm}) = 10^{-3} E c(\mu\text{N})$$

Nineteen snow samples were received by the University of Toronto. The samples were received on March 26, 1985 and stored in a freezer at -15°C . The weights of the samples varied between 580 and about 1200 grams. Three samples (Nos. 9, 23 and 50) were homogenized in solid state by breaking any lumps and mixing thoroughly. Measurements of conductivity and pH and titration were performed on melted portions. Later, the rest of the samples were melted for analyses.

All the other samples were melted in their totality, in plastic containers and homogenized by shaking. Conductivity, pH and acidity were determined immediately on portions of the liquid. The rest was filtered through fritted glass of medium porosity and stored in plastic containers inside a refrigerator until proceeding with the analysis.

Initial determinations were the conductivity, pH and the titrations. They were performed on the just-melted snow, previous to any further treatment of the sample. For these measurements, the CO_2 was prevented from entering the system or flushed out by passing Ar or N_2 gas through it. The reason for this procedure is that any dissolved CO_2 in the melted snow presumably originates by dissolution from the atmosphere, subsequent to the melting, and is therefore irrelevant to this study. Furthermore, the amount dissolved would depend on the time of contact (until reaching equilibrium) and on the local concentration of CO_2 in the air of the laboratory, which can be quite variable. It should be noted, however, that the measurement of pH and conductivity could only be affected very slightly by the CO_2 . For discussions on the influence of CO_2 in this project, refer to Appendix B; Appendix C for a discussion of the influence of CO_2 on conductivity and Appendix D for a discussion on the influence of CO_2 on measurement of weak acidity.

In the measurement of pH, the usual procedure was followed with the precautions mentioned by Galloway, et al (1979). The glass electrode used was of the Ross type (Orion 810200), particularly suitable for very dilute solutions because of its short equilibration time.

The cell constructed to measure pH is sketched in Figure E-1 of Appendix E. About 10 ml of melted snow are enough to cover the measur-

ing section of the electrode. Therefore, for samples 8, 23 and 50, about 10 g of snow were weighed in the cold room and introduced into the cell. Inert gas was passed to flush the air from the cell. The cell was then closed, taken out of the cold room, at 25°C and the pH measured.

For the rest of the samples, a small aliquot of liquid was introduced into the cell and the pH was measured. For $\text{pH} \geq 5$, Ar or N_2 was bubbled through the sample before the final reading was taken. This precaution becomes unnecessary at pH below 5, as explained in Appendix B (Presence of CO_2).

For the measurement of conductivity, the arrangement used is indicated in E-2 (see Appendix E). For samples 9, 23 and 50, cell and funnel were left to equilibrate temperatures in the cold room, the necessary amount of snow to fill the cell once melted was weighed and introduced into the funnel, inert gas was circulated for several minutes to flush all the air out of the cell and funnel, the stopcocks were closed and everything was taken out of the cold room. Once the snow was melted, it was transferred from the funnel to the cell and after thermostatzation at 25°C, the conductivity measurement is taken. For the rest of the samples, the funnel was substituted by a ground glass stopper, the liquid sample was introduced directly into the cell and the measurement was taken at 25°C.

Contact with CO_2 was avoided as much as possible, and in some of the samples, Ar or N_2 was bubbled through the sample to check on the absence of any influence. As explained in Appendix C, at pH 5, even an equilibrium concentration of CO_2 would only contribute about $0.2 \mu\text{S/cm}$.

In the measurement of acidity for each sample, a titration with NaOH (in most cases 2×10^{-4} N) was performed on 50 ml of freshly melted snow.

The presence of CO_2 will contribute to the weak acidity measured. This is irrelevant to the composition of the snow since CO_2 becomes dissolved after melting the sample and any possible content of HCO_3^- or $\text{CO}_3^{=}$ in the original snow would be altered. It is appropriate to eliminate it. Therefore, the following technique was adopted. A cell shown in Figure E-3 (in Appendix E) was prepared and used with a Ross electrode. The sample was introduced into the cell. An inert gas (N_2 or Ar) was bubbled through the liquid for a few minutes and the titration was performed while continuing to pass the inert gas. Bubbling was stopped to take each measurement so that the pH was determined with a quiescent solution. Bubbling also provided the necessary stirring. The titrations were followed to a pH of 8.8 to 9.0.

The usual ionic concentrations in snow are too low to obtain results of any precision with the analytical techniques currently available. These concentrations are sometimes only slightly above the detection limits which makes the determinations of doubtful precision and sometimes, even below the detection limit. For the present study, it was important to concentrate the samples after having been melted and filtered (once the portions used to determine pH, conductivity and acidity had been separated).

It was found that a simple concentration by boiling under a hood with an extractor was satisfactory. For the cations, a known volume of the sample (e.g. 300 ml) was put in a beaker. The sample was made to boil while stirring, covered with a ribbed watch glass until the volume

was sufficiently reduced. After rinsing the walls with small amounts of deionized water and homogenizing, the beaker with stirrer and concentrated solution was weighed again to 0.01 g so that the concentration factor f could be calculated. This concentrated sample was used for the determination of cations (Na^+ , K^+ , Mg^{++} , Ca^{++} and NH_4^+). As the pH of the samples was always between 4.7 and 5.5, this was considered a concentration in acid medium.

For the anions, the same procedure was followed, except that before concentrating, the sample was brought to a pH of 8.5 to 9.0 by the addition of the appropriate amount of 0.02 N NaOH. This amount could be calculated from the results of the acidity titration. The concentrated solution was used for the determination of inorganic anions (F^- , Cl^- , NO_3^- , $\text{SO}_4^{=}$) and organic anions (HCOO^- , $\text{CH}_3\text{CH}_2\text{COO}^-$ and $\text{C}_2\text{O}_4^{=}$). That the alkalization is essential to prevent losses was seen by the total absence of formate, acetate and propionate in the acid concentrations of samples containing these anions. Concentration factors between 3.18 and 7.35 were used (mostly 4 to 6), and these were seen to be sufficient to bring the concentrations to a range adequate for the analytical techniques. Once concentrated, the samples were stored in smaller plastic bottles in a refrigerator until analysis.

Blank tests were run with both deionized water and with water which washed several of the plastic bags which were used in the field. These blank samples were concentrated in an alkaline medium and tested for both inorganic and organic anions. They showed the complete absence of anions.

The cations Na^+ , K^+ , Mg^{++} and Ca^{++} were determined by an induc-

tively coupled plasma atomic emission spectrometry (ICP). The stipulated detection limits are:

Na	0.05 ppm or 2.0 μ N
K	0.05 ppm or 1.3 μ N
Mg	0.002 ppm or 0.17 μ N
Ca	0.002 ppm or 0.1 μ N

The concentrations of NH_4^+ were obtained with a specific ion electrode, which has a detection limit of 0.02 ppm or 10^{-6} N. Organic acids (other than oxalate, determined with the inorganic anions) were measured by ion chromatography using a special column (DIONEX-HPICE-A5-2). Formic, acetic and propionic acids could be detected in part of the samples, plus small peaks of an unidentified species in a few samples.

Ion chromatography was used to determine F^- , Cl^- , NO_3^- , $\text{SO}_4^{=}$ and C_2O_4 (oxalate) using a Dionex chromatograph with column HPIC-AS1. Appropriate standards with ionic concentrations in the range of 1 to 10 ppm were used for comparison. Approximate detection limits were:

F^-	0.01 ppm or 0.5 μ N
Cl^-	0.02 ppm or 0.5 μ N
NO_3^-	0.2 ppm or 3.0 μ N
$\text{SO}_4^{=}$	0.2 ppm or 4.0 μ N
$\text{C}_2\text{O}_4^{=}$	1 ppm or 8.0 μ N

RESULTS

Appreciable amounts of sediment were observed in the filters for many of the samples, (see Table 2; notable were No. 9 and 10); in particular, those coming from wooded areas contained litter from trees and soil. Samples No. 9 and No. 10 evolved small bubbles when shaken or boiled, which suggest the presence of surface active substances.

In the case of sample No. 10, an abnormally high content of sulphate was found in the analysis (105 μ N). Because this seemed incompatible with the initial determination of conductivity, it was concluded that an impurification had accidentally entered the sample; this was confirmed by a new measurement of conductivity. Thus, this sample was not considered in the subsequent analysis of data.

The detailed results of analysis of each of the snow cores are shown in Tables 2 to 6. The cores taken at each site are grouped together, so that common trends for interpretation of results may be undertaken. Acidity and conductivity were calculated for each core. The Gran plot technique was used to determine the strong and the weak acidity (McQuaker et al., 1983; Galloway et al., 1979). An example of such a plotting is included in Figure 3. Values of strong and weak acidity are listed in the third and fifth columns of Table 2. Expressing the strong acidity as a pH gave values consistent with the direct measurement of pH, within 0.1 to 0.2 units. These values are given in the fifth column of Table 2, as "pH calc". The observed vs the calculated values of conductivity are shown in Figure 4. There is reasonably good agreement in these two parameters except for samples 8 and 22, which have likely been contaminated.

Table 2. Acidity and conductivity measurement of the snow cores.

calc.	Bag No.	pH	Strong Acidity (μ N)	pH calc.	Weak Acidity (μ N)	K (μ S/cm)	K (μ S/cm)
<u>Haultain Lake Surface</u>							
	NW	52	5.06	11.6	4.94	12.5	5.8
		53	5.05	10.9	4.96	10.3	6.8
		54	5.03	11.7	4.93	9.0	6.7
	SW	33	4.92	13.2	4.88	15.2	8.4
		20	4.94	13.2	4.87	11.5	7.1
		39	4.96	13.4	4.87	11.5	6.9
	NE	42	4.88	16.0	4.78	18.4	8.3
		48	5.12	10.2	4.99	11.3	6.0
		50	5.47	3.3	5.48	6.4	9.1
	SE	22	4.74	13.8	4.87	6.5	11.4
		23	5.00	6.8	5.16	8.7	8.9
		24	5.15	12.9	4.89	9.2	5.7
<u>Tree Area</u>							
	NW	56	4.84	15.8	4.80	6.8	11.4
		58	4.99	14.2	4.85	15.3	7.9
	SE	27	4.88	12.3	4.91	3.4	9.3
		28	4.92	10.9	4.96	8.1	9.9
<u>Wollaston Lake Surface</u>							
	8D	5.05	9.2	5.04	12.8	10.3	14.4
	9D	5.45	6.4	5.19	28.4	11.2	11.6
	10D	5.10	6.6	5.19	5.2	7.1	-

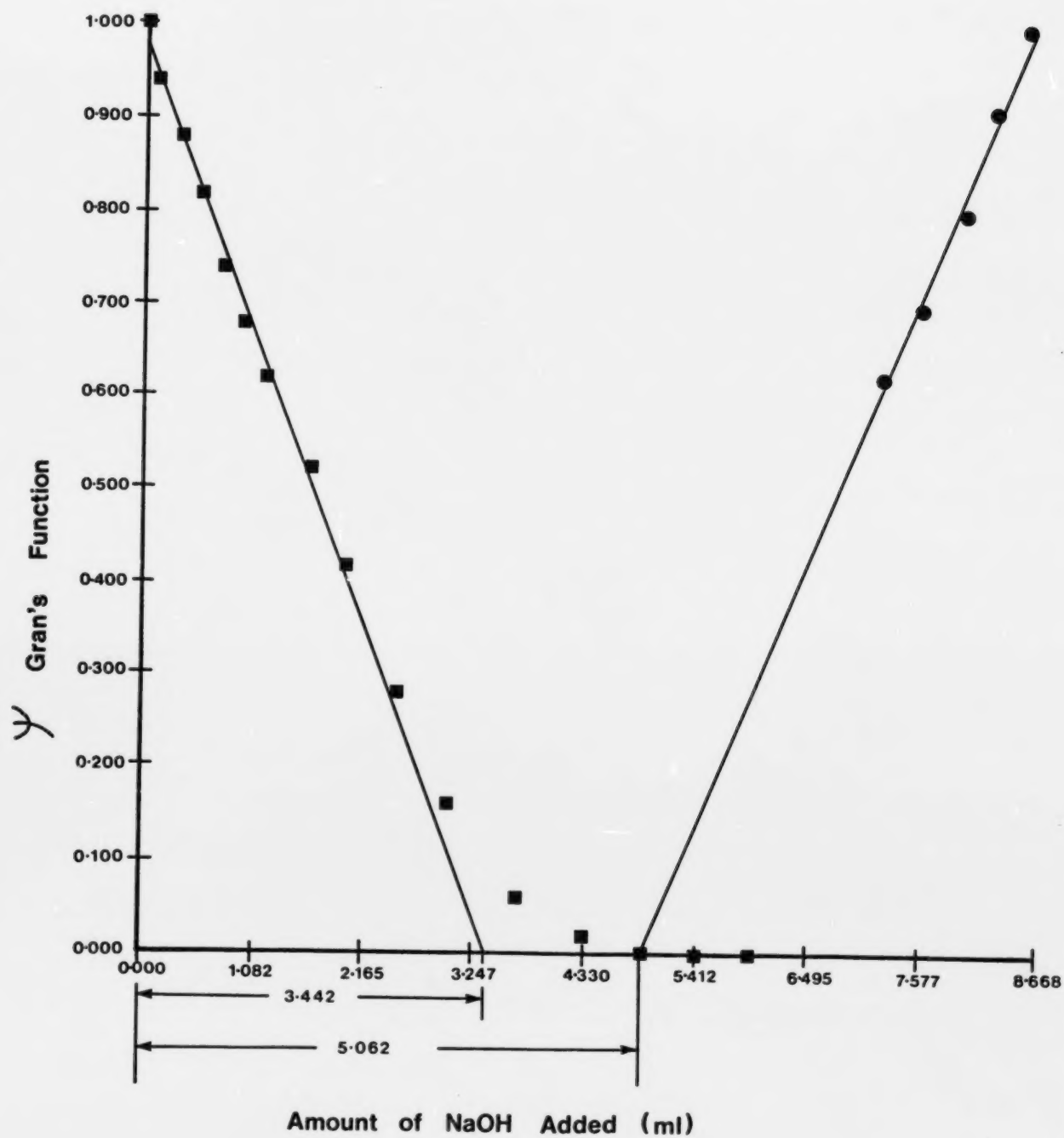


Figure 3. A Gran plot titration for snow sample No. 22.

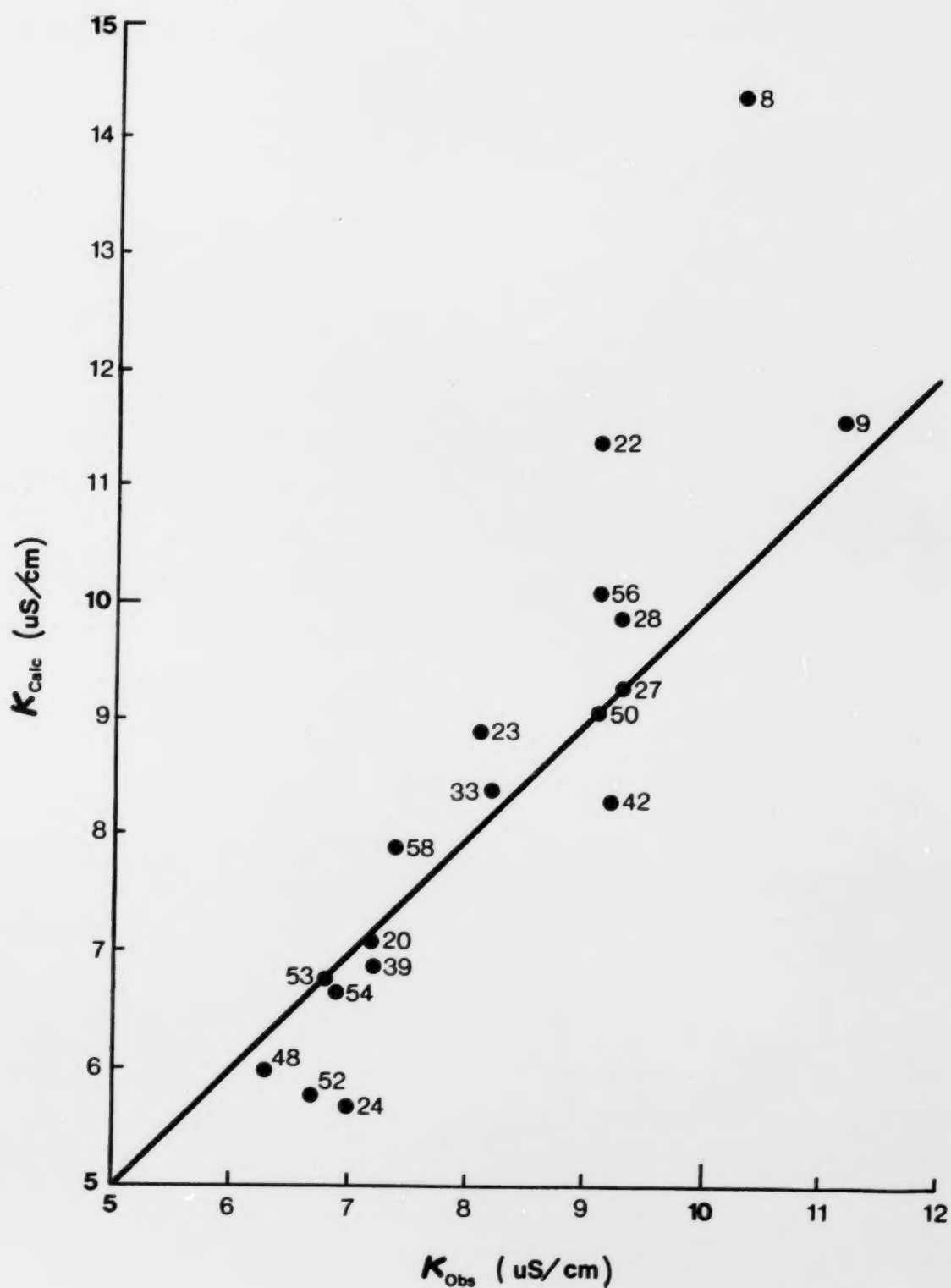


Figure 4. The observed conductivity vs the calculated conductivity.

The concentrations calculated for the samples of the inorganic cations are listed in Table 3. The concentrations of the hydrogen ions were calculated from the pH. The values of the hydrogen ion concentrations are also listed in the same table. It is worth noting here that small errors in the pH correspond to large errors in the hydrogen ion concentration. Thus, 0.1 unit of pH corresponds to a difference of 20% in the hydrogen ion concentration.

There is not one cation that dominates the total balance. However, hydrogen, ammonium, sodium and calcium are all important, and are present in the snow sample in roughly this order. For the snow collected from the tree areas near Haultain, the hydrogen ion is the most important one. At Wollaston, the calcium and sodium ion clearly dominate the cation structure. In the last column of this table is seen the total amount of inorganic cation observed in each core.

Table 4 gives the total anion structure of each of the snow cores, along with the total anion amount in the last column. It is apparent that chloride, sulphate and nitrate are the main controls of the anionic composition. Sulphate dominates the structure at every core location followed by nitrate, then chloride, in that order. Sulphates at Wollaston Lake were significantly higher than at Haultain Lake, while the nitrate composition was quite similar at both.

Table 3. The Concentration of Cations in the snow (μN)

	Bag No.	Na^+	K^+	Mg^{++}	Ca^{++}	NH_4^+	H^+	Σ^+
<u>Haultain Lake Surface</u>								
NW	52	4.6	0.9	1.6	4.0	5.9	8.7	25.7
	53	6.6	1.8	2.1	6.6	12.4	8.9	38.4
	54	3.4	1.0	1.8	4.4	13.1	9.3	33.0
SW	33	6.6	1.0	2.5	5.6	12.7	12.0	40.4
	20	4.8	1.5	1.6	5.7	5.1	11.5	30.2
	39	4.4	1.3	2.0	4.6	5.0	11.0	28.3
NE	42	4.2	0.6	2.6	6.5	9.0	13.2	36.0
	48	6.0	1.0	2.8	5.2	8.9	7.6	31.5
	50	16.4	5.4	11.0	20.3	12.4	3.4	68.9
<u>Tree Area</u>								
NW	56	10.4	2.8	3.4	10.9	4.1	14.4	46.0
	58	10.0	3.5	3.4	6.8	6.2	10.2	40.1
SE	27	6.4	3.3	2.3	7.0	5.9	13.2	38.1
	28	9.2	2.2	3.8	15.3	8.0	12.0	50.5
<u>Wollaston Lake Surface</u>								
	8	8.2	3.1	3.5	65.1	9.9	8.9	98.7
	9	23.2	6.7	17.1	29.4	4.2	3.6	84.1
	10	29.5	3.4	3.0	10.6	11.1	7.9	65.5

Table 4. The concentrations of inorganic anions (μN).

Bag No.		F^-	Cl^-	NO_3^-	$\text{SO}_4^{=}$	Σ^-
<u>Haultain Lake Surface</u>						
NW	52	0.3	2.3	8.1	11.1	21.8
	53	0.2	3.0	8.4	11.5	23.1
	54	0.2	3.4	8.4	11.4	23.4
SW	33	0.2	6.1	9.8	13.1	29.2
	20	0	2.6	8.5	12.8	23.9
	39	0	3.3	8.3	13.0	24.6
NE	42	0.2	3.3	13.0	13.8	30.3
	48	0	2.8	9.9	11.3	24.0
	50	0.5	16.5	12.1	17.0	46.1
SE	22	0.3	3.5	11.5	15.8	31.1
	23	1.0	11.3	9.6	14.9	36.8
	24	0	2.7	8.3	14.7	25.7
<u>Tree Area</u>						
NW	56	0.6	4.6	8.7	17.3	31.2
	58	0.7	7.4	8.8	15.8	32.7
SE	27	0.7	5.2	10.4	16.0	32.3
	28	0.5	5.9	11.0	24.5	41.9
<u>Wollaston Lake Surface</u>						
	8	0.4	5.9	5.6	23.1	35.0
	9	8.3	29.8	8.2	21.5	67.8
	10	5.4	8.0	7.4	-	-

The concentration of organic ions is given in Table 5. There were four main components identified. The organics confirmed in the samples were; formate, acetate, propionate and oxalate. The most dominant ion was propionate. An additional confirmation of this ion is seen in Appendix F. Propionate was present in nearly all of the samples. The other species appear in a rather spotty manner in most of the samples.

The snow cores from Wollaston have shown significant amounts of virtually all of the major organic ions. Column seven of Table 5 is the sum of the organics and column eight is the amount of dissociated species in the samples. The latter column refers to the amount of that particular species that is freely available to contribute to acidity.

A summary of the ion balance structure of each of the cores is given in Table 6. Total cation, anion and freely available organic ion are given in columns three to five. Column 6 is the inorganic anion deficit, whose average for all samples (12.9 μN) is stated at the bottom.

Column 7 gives the residual obtained when all ions are taken into account in the ionic balance; i.e., inorganic cations and anions, plus the organic anions corresponding to the dissociated fractions of the respective acids. These fractions were calculated taking into account the dissociation constant K of the acid and the pH of the sample. For example, if HA is the organic acid and its total concentration was determined as $[A]_t$, the anionic contribution (corresponding to the dissociated fraction) is:

$$[A^-] = \frac{K}{K + 10^{-\text{pH}}} = [A]_t$$

The average of the residuals in Column 7 is 3.0 μN , as stated at the bottom of the table.

If all the ions present in the solution have been determined, the sum of all the cations (in normality) should be equal to the sum of all the anions; i.e., the residual should vanish. Several remarks can be made here.

Table 5. The concentration of organic anions in the snow cores (μN).

<u>Bag No. Formate Acetate Propionate Oxalate -org.$\Sigma_{\text{tot.}}$ -org.$\Sigma_{\text{diss.}}$</u>							
<u>Haultain Lake Surface</u>							
NW	52	-	-	3.1	-	3.1	1.9
	53	-	-	4.4	-	4.4	2.6
	54	-	-	5.0	-	5.0	2.9
SW	33	2.2	-	2.6	-	4.8	3.5
	20	-	-	3.4	-	3.4	1.8
	39	-	-	4.1	-	4.1	2.2
NE	42	-	-	-	-	-	0
	48	-	-	-	-	-	0
	50	-	-	16.9	-	16.9	13.4
SE	22	3.9	1.8	49.9	-	55.6	25.2
	23	-	-	-	-	-	0
	24	-	-	2.7	-	2.7	1.7
<u>Tree Area</u>							
NW	56	4.9	1.5	24.1	2.4	32.9	19.0
	58	-	-	4.6	-	4.6	2.6
SE	27	4.1	1.8	26.8	-	32.7	18.2
	28	-	-	7.1	-	7.1	3.7
<u>Wollaston Lake Surface</u>							
	8	3.5	1.9	46.0	16.7	84.8	62.9
	9	2.7	-	18.5	-	21.2	17.2
	10	13.0	2.9	71.5	-	87.4	58.8

Table 6. A summary of the snow cores ion balances

		Σ_+	Σ_{-in}	$\Sigma_{-org, diss}$	$\Sigma_+ - \Sigma_{-in}$	$\Sigma_+ - \Sigma_{-in} - \Sigma_{-org, diss}$
<u>Haultain Lake Surface</u>						
NW	52	25.8	21.8	1.9	4.0	2.1
	53	38.4	23.1	2.6	15.3	12.7
	54	33.0	23.4	2.9	9.6	6.7
SW	33	40.4	29.2	3.5	11.2	7.7
	20	30.2	23.9	1.8	6.3	4.2
	39	28.3	24.6	2.2	3.7	1.5
NE	42	36.0	30.3	0	5.7	5.7
	48	31.5	24.0	0	7.5	7.5
	50	68.9	46.1	13.4	22.8	9.4
SE	22	44.8	31.1	25.2	13.7	-11.5
	23	51.5	36.8	0	14.7	14.7
	24	27.3	25.7	1.7	1.6	- 0.1
<u>Tree Area</u>						
NW	56	46.0	31.2	19.0	14.8	- 4.2
	58	40.1	32.7	2.6	7.4	4.8
SE	27	38.1	32.3	18.2	5.8	-12.4
	38	50.5	41.9	3.7	8.6	4.9
<u>Wollaston Lake Surface</u>						
	8	98.7	35.0	62.9	63.7	0.8
	9	84.1	67.8	17.2	16.3	- 0.9
	10	65.5	-	58.8	-	-
Average					12.9	3.0

Firstly, in spite of the increased accuracy of the analyses, the dispersion of residual data is still rather high. The standard deviation can be calculated to be $7 \mu\text{N}$.

Secondly, large positive residuals may suggest that not all the organic anions have been determined in this study. Negative residuals are less easy to explain, since positive organic ions seem improbable.

Thirdly, the fact that the average of the inorganic anion deficit ($12.9 \mu\text{N}$) is much larger than the average residual including organic anions ($3.0 \mu\text{N}$) seems to justify the assumption of a considerable contribution of organics.

The dissociated organic ions contribute in the range of 5 to 70 percent of the anions in solution. At the Haultain Site, dissociated organic acids contribute approximately 15 percent to the ion balance of each bag on a mean basis and at the Wollaston Site, these same organic ions contribute 58 percent to the ion balance on the mean of the core samples. It can also be seen that organic ions are more plentiful in the treed cores than at the lake surface cores at Haultain.

The non-dissociated part of the organic ion is equal to the total concentration, as determined by analysis, less the dissociated fraction. Two terms on the right hand side of Table 5 can be used to determine all of the acids present. This part will be included in the weak acidity. The latter may also include other acids not determined in the present analysis (e.g. dehydroabiatic acid).

$$\Sigma\text{-org, undiss.} = \Sigma\text{-org, tot.} - \Sigma\text{-org, diss.}$$

Finally, it should be pointed out that various tests were performed to check whether the presence of organic acids might be due to

impurities introduced by the sampling process. The plastic bags used to collect and send the snow samples were analyzed by infrared spectroscopy and found to be polyethylene which does not contain additives (in particular, organic acids). The chromatographic column used, tested with NaOH solutions of pH 11 and 12, did not appear to be a source of contamination.

DISCUSSION AND CONCLUSIONS

The analysis of snow samples on a routine basis from northern Saskatchewan is extremely delicate because of the low concentrations and the need to avoid time-consuming methods. Pre-concentration of the samples as done in this study, is time-consuming, but appears as a necessary step to bring the samples to a range of concentrations easily accessible for the current analytical techniques. Sufficient accuracy can then be attained and this allows a check in several ways for the consistency of the data. However, it must be taken into account that these checks, particularly through the ion balance and the conductivity, are performed with figures that accumulate the errors of many determinations.

Three of the analyzed samples correspond to one lake (Wollaston), while all the others belong to another lake (Haultain). While the first set seems to contain higher ionic concentrations than the second, it is also apparent that there is great variability for samples from the same lake area.

The following checks or comparisons have been made with the results indicated.

- a. The direct measurement of pH can be compared with that calculated from the strong acidity. This was generally satisfactory.
- b. The conductivity of the sample was calculated on the basis of ionic concentrations and equivalent conductances. The comparison was generally satisfactory, but two samples (Nos. 22 and particularly 8) showed considerable deviations.

- c. The ionic balance indicates clearly that organic acids cannot be ignored in the analyses. It is worth noting that the content in these acids is variable, and that the main constituent among them is the propionic acid which reached concentrations as high as 70 μN . Oxalic acid appears in considerable amount in only one sample (No. 8). Formic acid is clearly present in a number of samples, accompanied by a much weaker proportion of acetic acid. In a number of samples, organic acids appeared to be entirely absent. There is no organic ion contamination of the bags since all tests of this possibility proved negative.

In spite of the increased accuracy by sample concentration, considerable accumulated errors remain, reaching figures larger than 10 μN in four samples. Two of these cases (Bag numbers 23 and 53) correspond to an excess of cations; it is possible that these differences indicate that some undetected acid is also contributing anions. The two cases of large anion excess (Nos. 22 and 27) are more difficult to understand since undetected organic bases seem improbable.

Oxalic acid, which has been found in two samples, has a rather large $K_1 = 0.035$, and should be considered as a strong acid, i.e. totally dissociated (first dissociation) in the pH range of interest. It will also be partially dissociated in the second dissociation.

It is possible that part of the organic acids present are in the form of salts (e.g., sodium propionate). This is fully considered in Appendix F. In that case they will give no contribution to the acid-

ity, but the anions should be considered for the ionic balance. The possibility of salts of organic bases, such as alkaloids, has been considered improbable and not to be taken into account.

There are organics in the snow samples from northern Saskatchewan. They are present at almost every location. They are likely present as acids because they balance the excess cation. However, they are to some extent spotty in some samples; this is particularly the case at Haultain. Because of the fact that organics at Haultain seemed to be more prevalent in the samples taken from the treed area, this does imply that this area is a source region. If this were the case, we might well have expected one type of tree or soil to produce a measured organic acid impact, while the next tree or soil type a short distance away, produces an entirely different type of organic acid impact.

The dehydroabiatic acid deserves some attention. It has $K = 2 \times 10^{-6}$ at 20°C (Nyrén and Back, 1958). Therefore, it is expected that it will dissociate in the proportion of 9% at pH = 4.7, 17% at pH = 5 and 29% at pH = 5.3. This means that it might contribute appreciably to acidity if its concentration is high enough. Considering the results of Lunde et al. (1977) and the fact that conifers are abundant in the region under study, this acid should deserve attention in future studies.

In all discussions of contamination effects, it is known that sample 10 was clearly identified as having been contaminated likely in the laboratory. The nature and origin of this contamination within the laboratory environment has not been determined.

It should be noted that at Wollaston, the sulphates were significantly higher than at Haultain. This may, in part, be due to higher

deposition rates of sulphur since this area is closer to the Flin Flon smelter. It is at this site, however, that the organic ions are significantly influencing the chemistry.

The exact nature of the contamination of organics in the soil is uncertain. There are several mechanisms to consider. There is the direct contamination of the snow with falling particulate matter from the terrestrial system. In addition, there is the possibility that the various environment compartments (different types of trees for example) are emitting volatile organic compound which are being subsequently transformed to acids and salts in different degrees.

It is difficult to address the variability question, but this is one aspect of the snow chemistry research that keeps arising in a rather persistent manner. One would have expected a uniform, well-behaved pattern of concentration and deposition if the atmosphere was the source of these major ions. Hence, one would expect just as much acid in one snow core as in its neighbour. On the other hand, if one tree influences acidity in a different way from its neighbour, then it should be possible to see large variations between adjacent cores. In other words, variability suggests the influence of very local sources.

Fully dissociated organic ions may contribute from 5 to approximately 70 percent of the acidity of the snow pack. Thus, in considering this area, it is important to understand the influences of natural organic acid deposition to the background acidity. It is only by such an understanding of the acidification process that we can appraise the extent and impact of mineral acidic deposition which is known to originate from anthropogenic sources.

The fact that the amount of organic acid increases when the pH is too high in the concentration treatment also suggests that hydrolysable compounds of the organic acids (e.g., esters) are present in the snow (see Appendix F). However, preliminary gas chromatographic tests have confirmed qualitatively the presence of free propionic acid. The exact fraction present as free acids cannot be determined from these analyses because of the possible hydrolysis occurring during concentration. The problem of the organic contribution is therefore more complicated than just determining the presence and concentration of free acids. An investigation of the main organic compounds present in the snow should be done, with particular emphasis on those that may produce acids by decomposition.

RECOMMENDATIONS

1. The results obtained in this research indicate the presence in the snow of organic compounds that contribute directly to the free acidity of the snow. While organic acids have contributed to the snowpack acidity at both site locations, it was the Wollaston Site where significant and quantifiable amounts of organics were involved. Future studies must be concerned with areas similar to this. However, in the interest of efficiency, most studies in the immediate future should be concerned with increasing the quality of data from the Haultain Lake. Direct isolation of these organic acids should be done here.
2. It is recommended to extend this analysis to rain in northern Saskatchewan. Organic acids in the snow exert a significant control on acidity in northern Saskatchewan. A study should be considered to provide a similar type of analysis for rain. It is not at all certain that the rain should contain comparable amounts of organics. This is so because the scavenging rates and collection efficiencies are much different for rain.
3. Additional organic acids should be looked for at the various locations. This is particularly the case for dehydroabiatic acid which is likely present at some locations. This acid could make a significant contribution because of its dissociation constant.
4. It is recommended that the gas chromatograph-mass spectrometer system be used for scanning the main organic components, possibly using organic solvent extraction combined with a gas chromatograph-mass spectrometer system. Preliminary measurements with this system have indeed confirmed the presence of a free organic acid component in the snow.

5. It is recommended that other methods of concentration be applied. There is a need to clarify the form and possible action of these compounds. The possible hydrolysis effect to acid of the esters of these organic compounds must be considered carefully. Alternately, the samples might be concentrated by other techniques, such as freeze-drying or evaporation at reduced pressures, or by trace enrichment followed by ion chromatography of organic acids in the ion exclusion mode.

6. What is the concentration of organics in the thin surficial soil layers of this part of the province ? It is recommended that a small scale study be conducted of the soil and vegetation of the area to try and reveal the source of these organic acids. Since propionic acid is so abundant it might be useful to concentrate efforts on possible sources.

ACKNOWLEDGEMENTS

This work was conducted as a joint project between the University of Toronto and the Saskatchewan Research Council. Funding was provided by way of contract number 59(84-85) with the province of Saskatchewan.

The snow samples were collected from northern Saskatchewan by Environment Canada on their regular routine monitoring of the snow and lake water from this area of Canada.

REFERENCES

- Chameides, W.L. and D.D. Davis. 1983. Aqueous-phase of formic acid in clouds. *Nature* 304:426-429.
- Dawson, G.A., J.C. Farmer and J.L. Moyers. 1980. Formic and acetic acids in the atmosphere of the southwest U.S.A. *Geophysical Research Letters*, 7:725-728.
- Galloway, G.N., B.J. Cosby, Jr. and G.E. Likens. 1979. Acid precipitation: Measurement of pH and acidity. *Limnol. Oceanogr.* 24:1161-1165.
- Lunde, G., J. Gether, N. Guos and M.B.S. Lunde. 1977. Organic micro-pollutants in precipitation in Norway. *Atm. Env.* 11:1007-1014.
- McQuaker, N.R., P.D. Kluckner and D.K. Sandberg. 1983. Chemical analysis of acid precipitation: pH and acidity determinations. *Envir. Sci. Technol.* 17:431-435.
- Nicholas, H.J. 1973. Miscellaneous volatile plant products. Ch. 10 in L.P. Miller (ed). *Phytochemistry*. Vol. II. Van Nostrand Reinhold Co., pp. 445.
- Nyren, V. and E. Back. 1958. The ionization constant, solubility product and solubility of abietic and dehydroabietic acid. *Acta Chemica Scand.* 12:1516-1520.
- Shewchuk, S.R. 1985. An air mass back trajectory and precipitation chemistry analysis within northern Saskatchewan. SRC Technical Report No. 173.
- Shewchuk, S.R. 1983. A snowpack and surface water chemistry survey of small lakes in northern Saskatchewan. SRC Technical Report No. 155.
- Shewchuk, S.R. 1982. A snowpack chemistry study of small lakes in northern Saskatchewan. SRC Technical Report No. 137.
- Stevenson. 1967. Organic acids within the natural system. Given in a summary paper by M. Huang (1983). Dept. of Pedology. University of Saskatchewan.

APPENDICES

APPENDIX A

DISSOCIATION CONSTANTS OF SOME ORGANICS

APPENDIX A - DISSOCIATION CONSTANTS OF SOME ORGANIC ACIDS

Acid	$10^5 K$ (25°C)
Formic	17.7
Acetic	1.75
Propionic	1.34
Butyric	1.52
Oxalic	$K_1=3500$; $K_2=5.3$
Malonic	140
Succinic	6.4
Abietic	0.041
Dehydroabietic	0.2

APPENDIX B

INFLUENCE OF CO₂ ON pH MEASUREMENTS

APPENDIX B - INFLUENCE OF CO₂ ON pH MEASUREMENT

The Henry coefficient for the dissolution of CO₂ in water is

$$H = 0.0339 \text{ M atm}^{-1} \quad (25^\circ\text{C})$$

This coefficient gives the concentration of undissociated H₂CO₃, in molarity, per atmosphere of partial pressure of CO₂, in equilibrium conditions. i.e.,

$$H = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}}$$

The first dissociation constant of H₂CO₃ is

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} = 4.4 \times 10^{-7} \text{ M} \quad (25^\circ\text{C})$$

The constant for the second dissociation ($\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$) is very small (4.8×10^{-11}) and this dissociation can be ignored.

Once the CO₂ has been dissolved in a solution that already contains some acidity, it will contribute an additional amount to the acidity, i.e., an additional term to [H⁺], equal to [HCO₃⁻].

For the sake of making a numerical estimate, we assume a partial pressure of CO₂ as that found in the free atmosphere:

$$P_{\text{CO}_2} = 3.4 \times 10^{-4} \text{ atm}$$

Then we can calculate [HCO₃⁻] by using the constants H and K₁:

$$\begin{aligned} [\text{HCO}_3^-] &= \frac{[\text{H}_2\text{CO}_3]K_1}{[\text{H}^+]} = HK_1 \frac{P_{\text{CO}_2}}{[\text{H}^+]} \\ &= \frac{5.07 \times 10^{-12}}{[\text{H}^+]} \end{aligned}$$

where [H⁺] is the (total) H⁺ concentration when the solution is in equilibrium with P_{CO₂}.

If the solution does not have any other acidity than that due to the CO_2 ,

$$[\text{H}^+] = [\text{HCO}_3^-] = \sqrt{5.07 \times 10^{-12}} = 2.25 \times 10^{-6} \text{ M}$$

corresponding to the $\text{pH} = 5.65$ usually taken as a reference.

If the solution already had acidity prior to the dissolution of CO_2 , $[\text{H}^+]$ will be different. The following results can be obtained:

pH measured in presence of P_{CO_2} (in equilibrium)	pH measured in absence of CO_2
5.65	7.00
5.50	5.67
5.25	5.33
5.00	5.02
4.00	4.00

It can be seen that the influence of CO_2 is small in the range of interest; it decreases with pH , and from $\text{pH} = 5$ downwards, becomes entirely negligible.

APPENDIX C
INFLUENCE OF CO₂ ON CONDUCTIVITY MEASUREMENTS

APPENDIX C - INFLUENCE OF CO₂ ON CONDUCTIVITY MEASUREMENTS

Each dissociated H₂CO₃ contributes one HCO₃⁻ and one H⁺. Therefore, the additional conductivity K contributed by the dissolved CO₂ will be

$$\Delta K = \frac{[\text{HCO}_3^-] (\lambda_{\text{HCO}_3^-} + \lambda_{\text{H}^+})}{10^3} = 0.42 [\text{HCO}_3^-]$$

where $\lambda_{\text{HCO}_3^-}$ and λ_{H^+} are the equivalent ionic conductances of the two ions, and the values $\lambda_{\text{HCO}_3^-} = 70$, $\lambda_{\text{H}^+} = 350$ cm² S/eq. correspond to 25°C.

[HCO₃⁻] can be calculated as shown in Appendix A.

The following values may be quoted for illustration:

pH	[HCO ₃ ⁻] (M)	K (μS/cm)
3	5.2 x 10 ⁻⁹	0.0022
4	5.2 x 10 ⁻⁸	0.022
5	5.2 x 10 ⁻⁷	0.22
6	5.2 x 10 ⁻⁶	2.2

It may seem that CO₂ will only contribute sensibly to K when K is small and pH is in the high ranges.

APPENDIX D
CONTRIBUTION OF CO₂ TO WEAK ACIDITY

APPENDIX D - CONTRIBUTION OF CO₂ TO THE WEAK ACIDITY

By using the constant of hydrolysis for HCO_3^- and for CO_3^{2-} (respectively $K_{h1} = K_w/K_1 = 2.2 \times 10^{-8}$ and $K_{h2} = K_w/K_2 = 2.08 \times 10^{-4}$; where K_w = ionic product of water), it can be readily calculated that in the neutralization of H_2CO_3 , at the first equivalence point (corresponding to NaHCO_3 if NaOH is used) and at the concentration $1.15 \times 10^{-5} \text{ M}$ (corresponding to the H_2CO_3 in equilibrium with $P_{\text{CO}_2} = 3.4 \times 10^{-4} \text{ atm}$), the pH is equal to 7.7, while the second equivalence point will be reached for pH = 9.0. As the titration of the snow samples is carried to around pH ~ 8 to 9, the CO_2 will contribute to the weak acidity essentially as a monobasic acid. For the CO_2 concentration mentioned above, it would contribute by 11.5 μN . This is in the range of values for the total of other weak acids present in the snow. Therefore there is all the interest of eliminating CO_2 when performing the titration of strong and weak acidity. Otherwise, the weak acidity calculated would contain an unknown term (since the actual concentration is dissolved CO_2 is unknown) amounting to a large proportion of the calculated value.

If any bicarbonate is present in the original snow, its measurement is virtually impossible by titration, since it may be lost to the air as well as acquired from the air by dissolution of CO_2 , according to the conditions in which the titration is made. In the present measurements, any bicarbonate that might have been present, was eliminated by the bubbling of Ar or N_2 .

APPENDIX E
GLASSWARE USED TO ELIMINATE THE INFLUENCE OF CARBON DIOXIDE

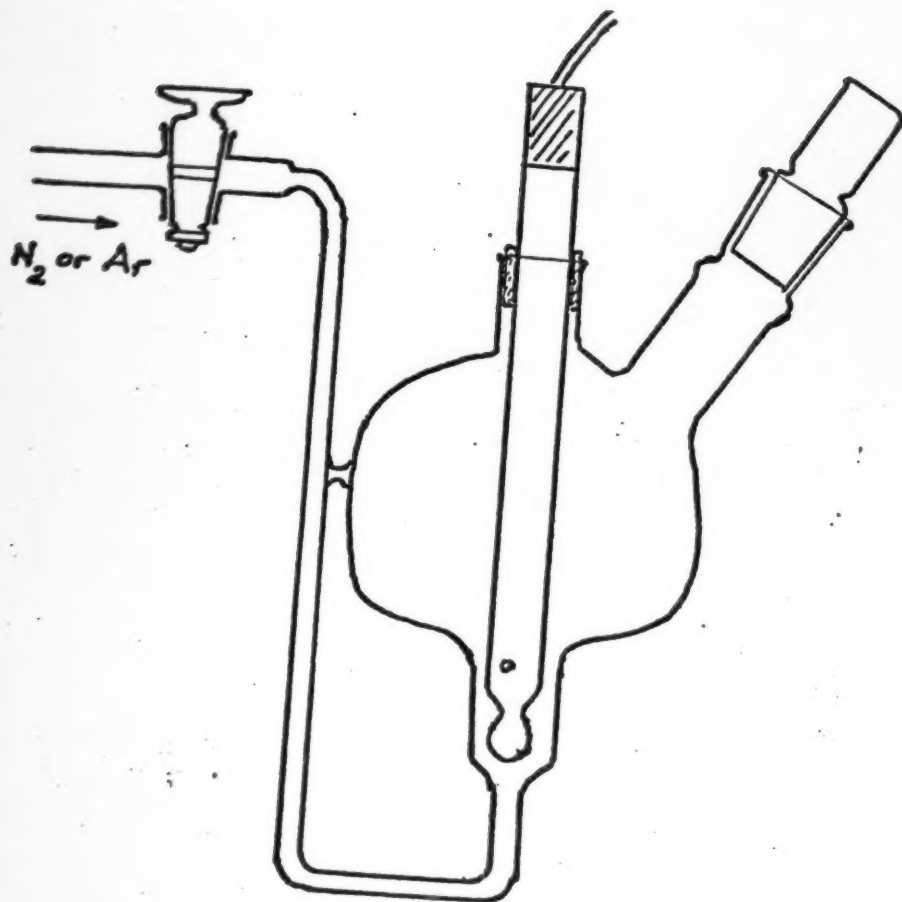


Figure E-1. Cell for determination of pH.

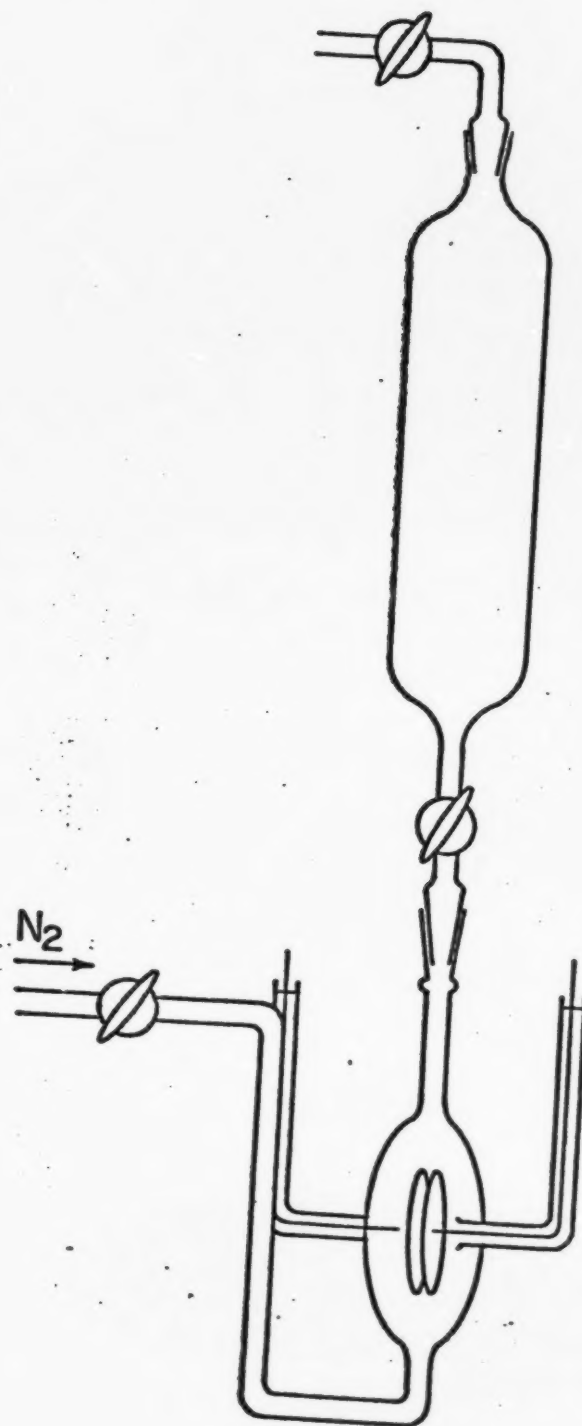


Figure E-2. Conductivity Cell.

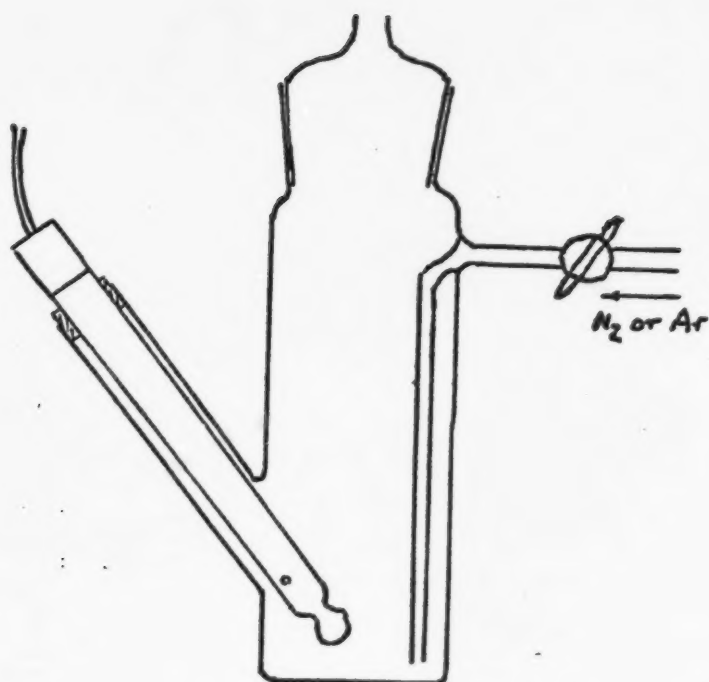


Figure E-3. Cell for titration of acidity.

APPENDIX F

A SEPARATE SERIES OF DETERMINATIONS ON A COMPOSITE SAMPLE
FROM HAULTAIN LAKE

One of the restrictions placed on the analysis of most samples in the main body of this report was the lack of sufficient sample volume to acquire adequate reproducibility in the analysis. Ten additional snow cores were involved in this study. Here, instead of conducting analysis on one core at a time, the snow core samples were collected together to form three large volume samples as indicated in Table F-1. The composite snow samples were made of cores from the west side of the lake (A), the east side of the lake (B) and the wooded areas of the lake (C). These samples were transferred from their plastic bags into plastic containers, melted, filtered through medium fritted glass funnels, and combined into three larger samples A, B and C. Considerable amounts of debris were observed in the samples from wooded areas.

Immediately after filtering, the measurements of pH, conductivity (at 25°C) and acidity (strong acidity and weak acidity, by the Gran method) were performed.

The results are given in Table F-1.

Table F-1 - Initial Measurements

Sample	pH	[H ⁺] (μ N)	Strong acidity (μ N)	pH _{calc}	Weak acidity (μ N)	K (at 25°C) (μ S/cm)	K calc (μ S/cm)
A	5.09	8.1	8.1	5.09	9.9	6.9	6.6
B	5.39	4.1	5.8	5.24	13.5	5.5	5.2
C	5.02	9.6	10.0	5.00	24.5	7.3	7.1

[H⁺] in the third column is calculated from the measured pH. pH_{calc} in the fifth column is the value that would correspond to the strong acidity. The last column shows the conductivity calculated from the sum of

the contributions of all inorganic ions (including H^+). Since larger volumes of samples were now available, larger concentrating factors were used (mostly between 15 and 25), so as to make possible a better accuracy in the determination of components.

In determinations for cations no additions were made. For the determination of anions, the pH was brought to various values, between 8.5 and 11. A blank test was run, concentrating at a pH = 9.6.

The concentrations of the cations Na^+ , K^+ , Mg^{++} and Ca^{++} were determined by atomic emission (Na^+ , K^+) and absorption (Mg^{++} , Ca^{++}). $[NH_4^+]$ was measured by a specific ion electrode. $[H^+]$ was calculated from the measured pH. These results are collected in Table F-2.

Σ_+ gives the sum of all cations.

Table F-2 - Inorganic Cations Concentrations (μN)

Sample	Na^+	K^+	Mg^{++}	Ca^{++}	NH_4^+	H^+	Σ_+
A	5.5	1.15	1.6	4.1	13.0	8.1	33.45
B	4.0	1.0	7.45	7.4	9.1	4.1	33.0
C	6.3	1.8	3.0	5.3	14.0	9.6	40.0

The inorganic anions were determined on the samples concentrated in alkaline medium, by ion chromatography. The results are collected in Table F-3.

Table F-3 - Inorganic Anions Concentrations (μN)

Sample	F^-	Cl^-	NO_3^-	$\text{SO}_4^{=}$	Σ_-	$\Sigma_+ - \Sigma_-$
A	0.6	2.3	12.1	12.8	27.8	5.65
B	0.6	2.4	10.0	14.0	27.0	6.1
C	1.25	2.6	8.55	11.6	24.0	16.0

is the sum of the four inorganic anions ($\Sigma_+ - \Sigma_-$) shows the inorganic ionic imbalance.

Using the technique of ionic chromatography in the ion exclusion mode, (ICE) was applied to the samples concentrated in alkaline medium. As in the previous sections, considerable concentrations of propionic acid were found, as well as small concentrations of formic acid, very small concentrations of acetic acid, plus small concentrations of an unidentified acid. Various tests indicated that none of the three following acids were involved: maleic, malonic, phthalic.

It was found that the concentrations of organic acid depended strongly on the pH. The concentration increased with pH. This suggests that, while free propionic acid (and other acids) may be present in the snow, there are probably derivatives (e.g., esters) that produce propionic acid by hydrolysis, during the concentration treatment.

In order to obtain an independent indication about the presence of free propionic acid, a qualitative analysis was performed with a gas chromatograph (Hewlett-Packard 5840A) on the non-concentrated melted snow. N_2 was passed through 15 ml of sample, to entrain vapour to a purging trap (7675A) with absorbent (TENAX); subsequent desorption by

heat provides the sample for injection into the GC. The results indicated the presence of free propionic acid in the three samples, A, B and C. However, it could not be quantified with this procedure. The problem of organic compounds in the snow requires further investigation to quantify the free acid levels.